



# Thermal Analysis

Vol. 2    Inorganic Chemistry/Metallurgy  
          Earth Sciences  
          Organic Chemistry/Polymers  
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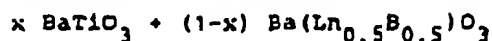
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## THERMAL BEHAVIOUR OF COMPOSITIONS IN THE SYSTEMS



V.S. Chincholkar\* and A.R. Vyawahare

Department of Chemistry, Institute of Science, Nagpur

ABSTRACT

The effect of temperature on the dielectric constant ( $\epsilon$ ),  $\tan \delta$  (loss tangent) and the ferroelectric properties of compositions in the systems  $x \text{ BaTiO}_3 + (1-x) \text{ Ba}(\text{Ln}_{0.5}\text{B}_{0.5})\text{O}_3$  ( $0 \leq x \leq 1$ ,  $\text{Ln}^{3+}$  = a rare earth cation and  $\text{Y}^{3+}$ ,  $\text{B}^{5+} = \text{Ta}, \text{Nb}, \text{V}$ ) reveal that in the  $\text{Ta}^{5+}$  system at  $x = 0.8$ , the  $\epsilon_{\text{max}}$  ( $\epsilon$  at  $T_c$ ) and  $T_c$  (the Curie-point) exhibit an increasing trend with decreasing ionic radii of the  $\text{Ln}^{3+}$  ions, whereas in the analogous  $\text{Nb}^{5+}$  system, an almost linear behaviour has been observed. In the  $\text{V}^{5+}$  system, the pure phases ( $x = 0$ ) exhibit increasing trend of  $\epsilon_{\text{max}}$  and  $T_c$  values with decreasing rare earth cation size. Phases with  $x = 0.8$ , exhibit a break at  $\text{Nd}^{3+}$  in  $\epsilon_{\text{max}}$  values, in contrast to an increasing trend in  $T_c$  values with decreasing rare earth cation size. Similar behaviour is observed for the polarization data. The increasing trend in the  $T_c$  values in the direction  $\text{Ta}^{5+} - \text{Nb}^{5+} - \text{V}^{5+}$  at  $x = 0.8$  is perhaps reminiscent of the nephelauxetic effect.

The  $T_c$  values for these first order transitions have been confirmed by recording DTA curves against inert  $\alpha\text{-Al}_2\text{O}_3$ , the enthalpy change, however, being appreciably low in the present series.

INTRODUCTION

Recently emphasis has been placed on laser research and a concentrated effort has brought new and improved materials which can be used as hosts for transition. An important part of this effort has been directed towards finding potential laser materials having fluorescent energy states with long life times. In order to determine if symmetry conditions in

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crystals also affect the life time of rare earth ion fluorescence, a series of ordered perovskite compounds having the general formula  $A(B'_{0.5}B''_{0.5})O_3$  were studied [1]-[7]. However, temperature effects and doping characteristics were not studied. The present work concerns with the formation and the thermal characteristics of compositions in the systems  $x BaTiO_3 + (1-x) Ba(Ln_{0.5}B_{0.5})O_3$  where  $0 \leq x \leq 1$ ,  $Ln^{3+}$  = a rare earth cation and  $B^{5+} = Nb^{5+}, Ta^{5+}$  and  $V^{5+}$ .

#### EXPERIMENTAL PROCEDURE

The compositions were prepared by the solid state reaction of the parent compounds (carbonates, oxides) at high temperature as described elsewhere [8], [9]. Room temperature X-ray structure was determined using Debye-Scherrer camera (14 cm diameter) and nickel-filtered  $Cu-K\alpha$  radiation. Temperature effects on the dielectric constant (capacitance) and loss tangent ( $\tan \delta$ ) were measured using a 716-C GR capacitance bridge together with type 1340-B type audiobeat frequency generator and 1231-B type u null detector and amplifier with 1231  $P_5$  type variable filter in a sample holder designed in this laboratory [10].

Modified [11] Sawyer-Tower type circuit was used to record hysteresis loops as a function of temperature in the above sample holder and a MOM Derivatograph was used to record DTA curves against  $\alpha-Al_2O_3$  as reference.

#### RESULTS AND DISCUSSION

Tables 1-3 show the room temperature  $\epsilon$  values as also the  $\epsilon_{max}$  and the Curie-point ( $T_c$ ) values evaluated from the capacitance measurements for compositions in the various systems. The temperature study was restricted to  $x = 0.8$  compositions in the  $Ta^{5+}, Nb^{5+}$  systems and over the entire composition range in the  $V^{5+}$  system which exhibited the transition in the whole range of compositions. Table 4 shows these parameters at  $x = 0$  for compositions in the  $V^{5+}$  system. In all the sy-

stems, an increase in  $\epsilon_{max}$  with decreasing rare earth content of the lanthanide

$\epsilon_{max}$ ,  $P_5$  and  $T_c$  values

#### Composition

$Ba(La_{0.1}Ta_{0.1}Ti_{0.8})$   
 $Ba(Nd_{0.1}Ta_{0.1}Ti_{0.8})$   
 $Ba(Sm_{0.1}Ta_{0.1}Ti_{0.8})$   
 $Ba(Gd_{0.1}Ta_{0.1}Ti_{0.8})$   
 $Ba(Dy_{0.1}Ta_{0.1}Ti_{0.8})$   
 $Ba(Y_{0.1}Ta_{0.1}Ti_{0.8})$

$\epsilon_{max}$ ,  $P_5$  and  $T_c$  values

$Ba(La_{0.1}Nb_{0.1}Ti_{0.8})$   
 $Ba(Nd_{0.1}Nb_{0.1}Ti_{0.8})$   
 $Ba(Sm_{0.1}Nb_{0.1}Ti_{0.8})$   
 $Ba(Gd_{0.1}Nb_{0.1}Ti_{0.8})$   
 $Ba(Dy_{0.1}Nb_{0.1}Ti_{0.8})$   
 $Ba(Y_{0.1}Nb_{0.1}Ti_{0.8})$

$\epsilon_{max}$ ,  $P_5$  and  $T_c$  values

$Ba(La_{0.1}V_{0.1}Ti_{0.8})$   
 $Ba(Nd_{0.1}V_{0.1}Ti_{0.8})$   
 $Ba(Sm_{0.1}V_{0.1}Ti_{0.8})$   
 $Ba(Gd_{0.1}V_{0.1}Ti_{0.8})$   
 $Ba(Dy_{0.1}V_{0.1}Ti_{0.8})$   
 $Ba(Y_{0.1}V_{0.1}Ti_{0.8})$

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stems, an increasing trend in  $\epsilon_{\max}$  as also  $T_c$  is observed with decreasing rare earth cation size, and is perhaps reminiscent of the lanthanide contraction.

Table 1

$\epsilon_{\max}$ ,  $P_s$  and  $T_c$  values for compositions in the  $Ta^{5+}$  system

Composition	$\epsilon_{25^\circ C}$	$P_s$ ( $\mu C/cm^2$ )	$\epsilon_{\max}$	$T_c$ ( $^\circ C$ )
Ba(La <sub>0.1</sub> Ta <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	200	4.5	780	85
Ba(Nd <sub>0.1</sub> Ta <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	250	6.0	850	90
Ba(Sm <sub>0.1</sub> Ta <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	342	8.1	1050	92
Ba(Gd <sub>0.1</sub> Ta <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	480	8.5	1120	96
Ba(Dy <sub>0.1</sub> Ta <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	530	8.9	1400	100
Ba(Y <sub>0.1</sub> Ta <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	580	9.6	1830	110

Table 2

$\epsilon_{\max}$ ,  $P_s$  and  $T_c$  values for compositions in the systems  $Nb^{5+}$

Ba(La <sub>0.1</sub> Nb <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	232	5.3	580	90
Ba(Nd <sub>0.1</sub> Nb <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	260	6.2	900	100
Ba(Sm <sub>0.1</sub> Nb <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	290	8.4	1100	107
Ba(Gd <sub>0.1</sub> Nb <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	380	9.2	1220	110
Ba(Dy <sub>0.1</sub> Nb <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	415	9.8	1350	115
Ba(Y <sub>0.1</sub> Nb <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	530	10.2	1600	118

Table 3

$\epsilon_{\max}$ ,  $P_s$  and  $T_c$  values for compositions in the  $V^{5+}$  system

Ba(La <sub>0.1</sub> V <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	170	4.5	1100	93
Ba(Nd <sub>0.1</sub> V <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	225	3.5	840	124
Ba(Sm <sub>0.1</sub> V <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	280	7.5	1130	130
Ba(Gd <sub>0.1</sub> V <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	350	8.2	1290	135
Ba(Dy <sub>0.1</sub> V <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	480	8.2	1600	135
Ba(Y <sub>0.1</sub> V <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	530	12.2	2200	125

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Table 4  
 $\epsilon_{\max}$ ,  $P_s$  and  $T_c$  values for compositions in the  $v^{5+}$  system at  $x = 0$

Composition	$\epsilon_{\max}$	$P_s$	$T_c$
Ba(La <sub>0.5</sub> V <sub>0.5</sub> )O <sub>3</sub>	60	--	--
Ba(Nd <sub>0.5</sub> V <sub>0.5</sub> )O <sub>3</sub>	20	7.8	260
Ba(Sm <sub>0.5</sub> V <sub>0.5</sub> )O <sub>3</sub>	30	10.7	500
Ba(Gd <sub>0.5</sub> V <sub>0.5</sub> )O <sub>3</sub>	35	11.3	850
Ba(Dy <sub>0.5</sub> V <sub>0.5</sub> )O <sub>3</sub>	25	12.5	1020
Ba(Y <sub>0.5</sub> V <sub>0.5</sub> )O <sub>3</sub>	40	17.9	1250

Covalency of the B-O bond is reported [12] to increase with decreasing rare earth cation size and may be responsible for the above occurrence. The behaviour, however, is linear in case of Nb<sup>5+</sup> and non-linear in the case of Ta<sup>5+</sup>, V<sup>5+</sup>.

Table 5 shows the  $T_f$  and  $\Delta H$  values as evaluated from the DTA curves, for some representative samples.

Table 5

Composition	$T_f$ (°C)	$\Delta H$ (cal mole <sup>-1</sup> )
Ba(La <sub>0.1</sub> Ta <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	80	25
Ba(La <sub>0.1</sub> Nb <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	90	45
Ba(La <sub>0.1</sub> V <sub>0.1</sub> Ti <sub>0.8</sub> )O <sub>3</sub>	95	65

A glance at the  $\Delta H$  values reveal dilution of the  $\Delta H$  value of the 120°C transition of BaTiO<sub>3</sub> (46 cal/mole) [13] by the addition of Ta<sup>5+</sup> phases, no change with addition of Nb<sup>5+</sup> phases and a substantial increase with incorporation of V<sup>5+</sup> phases.

Another significant result of the present study is the observation of increasing  $T_c$  ( $T_f$ ) values with decreasing B<sup>5+</sup> radii, keeping the Ln<sup>3+</sup> ion fixed, in the sequence Ta<sup>5+</sup>-Nb<sup>5+</sup>-V<sup>5+</sup>.

Considering the energy level diagram of an octahedrally surrounded metal ion with configuration (np)<sup>6</sup>, we expect Ta<sup>5+</sup> to

be more ionic this the elec will be less justified by these ions T Jørgensen has that the elec Nb<sup>5+</sup>-V<sup>5+</sup> and transition me cal bond beco Our results a

Fifth ionizati

Ion

V<sup>5+</sup>

Nb<sup>5+</sup>

Ta<sup>5+</sup>

[1] F. Galasso  
Report OAF

[2] F. Galasso  
81 (1959)

[3] F. Galasso  
83 (1961)

[4] F. Galasso

[5] F. Galasso

[6] F. Galasso

[7] F. Galasso

[8] V.S. Chinc

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be more ionically bonded than  $Nb^{5+}$  and  $V^{5+}$ . As a result of this the electron density in the  $t_{2g}$ -orbital of the  $Ta^{5+}$  ion will be less than that in the case of  $Nb^{5+}$ ,  $V^{5+}$ . This is also justified by considering the fifth ionization potential of these ions (Table 6) which also increases in this sequence. Jørgensen has concluded from the electron transfer spectra that the electron affinity increases in the sequence  $Ta^{5+} - Nb^{5+} - V^{5+}$  and from the reduced Racah parameters of several transition metal ions (nephelauxetic effect) that the chemical bond becomes more covalent in the sequence 5d-4d-3d group. Our results are consistent with the observations of Jørgensen.

Table 6

Fifth ionization potential and electron configuration of  $B^{5+}$  metal ions

Ion	Electron configuration	$I_5$ (eV)
$V^{5+}$	$3s^2 3p^6$	65
$Nb^{5+}$	$4s^2 4p^6$	52
$Ta^{5+}$	$5s^2 5p^6$	45

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\* Present address: Forensic Science Laboratory, Bombay-8

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